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Research Article

ASSESSMENT OF THE ELECTRICITY GENERATION, DESALINATION, AND WASTEWATER TREATMENT EFFICIENCIES OF A MICROBIAL DESALINATION CELL OPERATING WITH ELECTROLYTE DILUTION AS PH CONTROL MEASURE

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ABSTRACT

In this study, the dilution of anolyte and catholyte as a pH control measure in a newly developed microbial desalination cell (MDC) was explored. Also, the effects of dilution on the newly developed MDC's electricity generation, desalination and wastewater treatment efficiencies were assessed against a three-chamber MDC which used potassium phosphate buffer for pH control. On the average, the newly developed MDC exhibited a lower buffer capacity (pH change of 1.73 ± 0.06) as compared to the relatively higher buffer capacity (pH change of 1.49 ± 0.07) of the three-chamber MDC. However, the newly developed MDC produced a higher desalination efficiency of 50.01% compared to the 46.66% produced by the three-chamber MDC and a higher power density of 0.62 ± 0.13 W/m^3 than the 0.35 ± 0.70 W/m^3 produced by the three-chamber MDC. It's COD reduction efficiency (63.21%) was also higher than the 42.81% produced by the three-chamber MDC.

Keywords : Exoelectrogens, desalination, voltage, current, COD

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1. INTRODUCTION

Anticipated water shortages in the future have made wastewater reuse and desalination important considerations to adopt [1]. However, present-day wastewater treatment and desalination technologies are high energy consumers requiring lots of energy for their operations [2]. In the wake to develop cheaper wastewater and desalination technologies, the microbial desalination cell (MDC) technology was developed for simultaneous wastewater treatment, desalination, and electricity generation [3]. However, maintaining the pH of anolytes and catholytes of MDCs around neutral conditions (pH 7) is a problem preventing the scale-up of this technology.

pH changes in the anodes and cathodes chambers of MDCs militate against their optimal operations. During the operation of an MDC, the pH of anolytes reduce to acidic conditions while those of catholytes increase to alkaline conditions. The slower movement of protons to electrons is responsible for pH drops in anolytes [2] while pH increment in cathodic solutions is caused by the consumption of protons and oxygen reduction [4]. Several research works have been conducted to solve this pH problem. These include Qu et al [4] work where recirculation of electrolytes between the anode and cathode chambers was used for pH control. This intervention could maintain anolyte pH at 6.7 ± 0.1 and catholyte pH at 6.9 ± 0.1 in a 50 mM phosphate buffer solution (PBS) for 20 hours. In a similar development, Davis et al [5] used the catholyte of a previous experiment to control anolyte pH imbalances in a multi-anode bench-scale microbial desalination cell. In this work, the addition of 75 mM of catholyte increased the initial pH of anolyte from 7.17 ± 0.03 to 8.12 ± 0.4. However, anolyte pH at the end of the 10-hour treatment cycle could drop to 5.0 ± 0.1 [5]. Luo et al [6] also used the recirculation of buffered electrolytes between electrode chambers and a 500 ml reservoir to regulate the pH of anolytes and catholytes between pH 7 and 8 for a period of 110 hours.

In another development, Forrestal et al. [7] replaced the anion exchange membrane that is usually used to separate the anode chamber from the desalination chamber in an MDC with a cation exchange membrane in a microbial capacitive desalination cell (MCDC). This was done to allow the flow of accumulated H^+ ions from the anode chamber to the cathode chamber. This strategy caused a slight rise (1.5 units from 7.0 ± 0.2) in catholyte pH over a desalination cycle (20 hours). On the other hand, the slight drop (0.2) in anolyte pH was attributed to the good buffer capacity of the $NaH_2PO_4.H_2O/Na_2HPO_4$ buffer in the anolyte [7]. Also relying on buffers for pH control, Kokabien and Gude [8] used a strong potassium phosphate buffer (KH_2PO_4/K_2HPO_4) to control anolyte pH around 6.4 and 6.7 and a combination of potassium phosphate buffer and the replacement of catholyte with anolyte to control catholyte pH around pH 6.4 and 9.7 for a total of 290 hours.

This notwithstanding, the pH control measures employed in the enlisted studies are expensive considering energy input and the high cost of chemicals. Thus, the search for equally effective but relatively inexpensive pH control measures continues unabated. In this present research, the potential of dilution as a pH control measure was investigated. To this, two additional chambers (neutralization chambers) containing distilled water were attached to a conventional three-chamber MDC to provide the dilution effect to anolytes and catholytes. This setup was called the newly developed MDC. The dilution effect of the neutralization chambers was based on water osmosis resulting from the concentration difference between anolytes and catholytes, and the distilled water in the neutralization chambers of the newly developed MDC. The effect of dilution on the pH, electricity generation, desalination, and wastewater treatment performances of this newly developed MDC was assessed using an MDC (three-chamber MDC) which relied on potassium phosphate buffer for pH control as a benchmark. The performances of the neutralization chambers for pH control was assessed against potassium phosphate buffer because phosphate buffers are standard buffers used to control pH in MDCs. Even in MDCs employing recirculation for pH control, potassium phosphate buffers have been used to aid pH control [5-8].

2. RESULTS AND DISCUSSIONS

2.1 pH changes in MDCs under Investigations

The pH of anolytes of both MDCs decreased (Table 1) across batch cycles while that of the catholytes increased (Table 2). The continuous decreases in anolyte pH across the batches were attributed to the increase in the concentration of H^+ ions within electrode brushes and biofilms and then in anolytes. This was possibly the case because; the same electrodes (colonized by biofilms) were used in all batch cycles. The relatively slow movement of buffers into biofilms compared to the faster proton production by bacteria action causes the immediate environment of biofilms to be more acidic than anolytes [5]. Thus, it might not be advisable to use the same electrodes with formed biofilms for more than one batch cycle of experiment. Increments in catholyte pH on the other hand were associated with proton consumption. Higher pH in the cathode chamber contributes to electrode potentials losses [4]. This notwithstanding, in an earlier study it was reported that an increase in catholyte pH is not as problematic as an increase in anolyte pH considering the negative effects anolyte pH changes have on system performances [4].

Comparing the pH changes recorded from the MDCs, it was realized that, the potassium phosphate buffer stabilized pH better than the neutralization chambers of the newly developed MDC (Table 1 and 2). The comparatively lower performance of the neutralization chambers in pH control was probably because water flux into the anode and cathode chambers of the newly developed MDC was small. This was shown in the small volume increments in anolytes and catholytes from 220 ml to 222 and 224 ml respectively. The use of a forward osmosis membrane could have increased the quantity of water fluxed across membranes. This however would have led to the flooding of anolytes and catholytes and thus serve the purpose of water abstraction [9, 10] instead of dilution for pH control.

Another reason attributed to the relatively lower pH control performance of the neutralization chambers was that the newly developed MDC produced a higher current density of 1.75 ± 0.11 A/m^3 as compared to the 1.24 ± 0.30 A/m^3 produced by the three-chamber MDC. The higher electricity production of the newly developed MDC implied that more H^+ and OH^- ions were produced in the anolytes and catholytes respectively thus creating the need for a stronger buffer/buffering mechanism to keep pH within neutral conditions.

Nevertheless, comparing the pH changes reported in earlier studies were no buffers were used for pH control to the pH stabilization effect (Table 1 and 2) of the neutralization chambers, dilution through water osmosis could be stated to have a good potential for pH control. For instance, Lu et al [2] reported that, when an MDC was not buffered, its anolyte pH could decrease from pH 7 to 5.7. Also, Ping and He [11] reported that when no buffer was added to the catholyte in their study, pH could rise to 12. Davis et al [5] also reported of catholyte pH as high as 12.8 ± 0.3 when no buffer was added to the catholyte of the MDC they studied.

Table 1. pH changes in anolyte

		Batch 1	Batch 2	Batch 3
Cell Type	Initial pH	Final pH	Final pH	Final
3C MDC	6.99 ±0.01	5.56±0.25	5.48±0.12	5.32±0.16
5C MDC	7.08 ±0.02	5.42±0.11	5.29±0.14	5.1±0.02

Where 3C MDC is three-chamber MDC with phosphate buffer; 5C MDC is the newly developed MDC with neutralization chambers

Table 2. pH changes in catholyte

		Batch 1	Batch 2	Batch 3
Cell Type	Initial pH	Final pH	Final	Final
3C MDC	7.04±0.03	8.34±0.33	8.47±0.53	8.63±0.35
5C MDC	7.12±0.01	8.65±0.18	8.78±0.01	8.89±0.16

2.2 Assessment of the electricity generation, desalination, and wastewater treatment performance efficiencies of the MDCs

2.2.1 Electricity Production

The peak voltages produced by the three-chamber MDC and that produced by the newly developed MDC were 282.91 ± 0.09 (Fig 2) and 343.57 ± 0.25 mV (Fig 1) respectively. This translated to 0.283 and 0.345 mA of electric current for the respective MDCs. These currents produced were appreciable especially when compared to the 0.15 mA reported by Zhang et al [12]. The higher peak voltage of the newly developed MDC was attributed to the possible contribution of ion migration to electricity production. That is, the possible migration of ions along with water flux from the neutralization chambers into adjacent chambers possibly contributed to voltage production. Electricity production in MDCs principally results from the degradation and release of electrons from substrates by exoelectrogens. This notwithstanding, the movement of ions across selective membranes also contributes to electricity production [10], thus its implication as a contributor to the higher electricity generation in the newly developed MDC. Voltage profiles of the MDCs in this study showed a trend of an initial peak, and then a decline across experiments (Fig 1 and 2).

A similar trend was reported by Cao et al [3] and they associated their observation to increments in ohmic resistance due to conductivity changes. In this study too, changes in conductivity in the middle chamber were observed with conductivity reducing from an initial of 53.5 mS/cm to 26.75 ± 3.75 mS/cm in the newly developed MDC and from 53.5 mS/cm to 28.54 ± 3.34 mS/cm in the three-chamber MDC (Table 3). There were corresponding increases in the internal resistances of the MDCs in respect of conductivity reductions. The internal resistance of the three-chamber MDC increased from 41 to 48 Ω and that of the newly developed MDC increased from 48 to 90 Ω (Fig. 3). The higher internal resistance of the newly developed MDC was attributed to its' use of more (five) ion-exchange membranes. It was also observed that, as the pH of anolytes decreased, maximum voltages also decreased. This was expected because the MDC technology depends on exoelectrogens and therefore any negative effect on these bacteria will result in voltage drops [5, 13]. Consequently, it was sound to conclude that, reductions in anolyte pH contributed to the observed decreasing trend in voltages across batches.

Table 3. Changes in electrical conductivities and Peak voltages produced from the MDCs

CELL TYPE	**Batch 1**		**Batch 2**		**Batch 3**	
	EC (mS/cm)	Peak voltage (mV)	EC (mS/cm)	Peak voltage (mV)	EC (mS/cm)	Maximum voltage (mV)
5C MDC	46.86±0.53	343.57±0.25	37.46±2.02	332.56±0.51	26.75±3.75	332.38±0.14
3C MDC	47 ± 0.42	283.01±0.09	35.20±4.08	272.03±0.17	28.54±3.34	271.71±0.06

Where EC is - Electrical conductivity

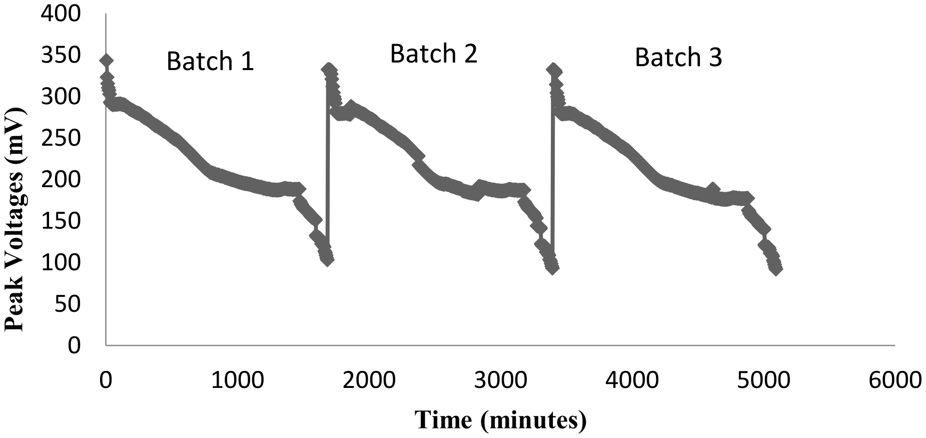

Fig.1. Voltage profiles of the newly developed MDC

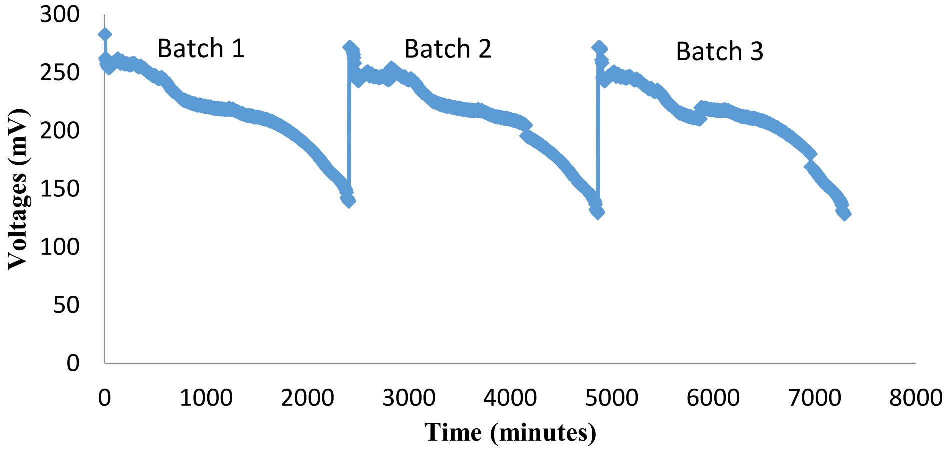

Fig.2. Voltage profiles of the three-chamber MDC

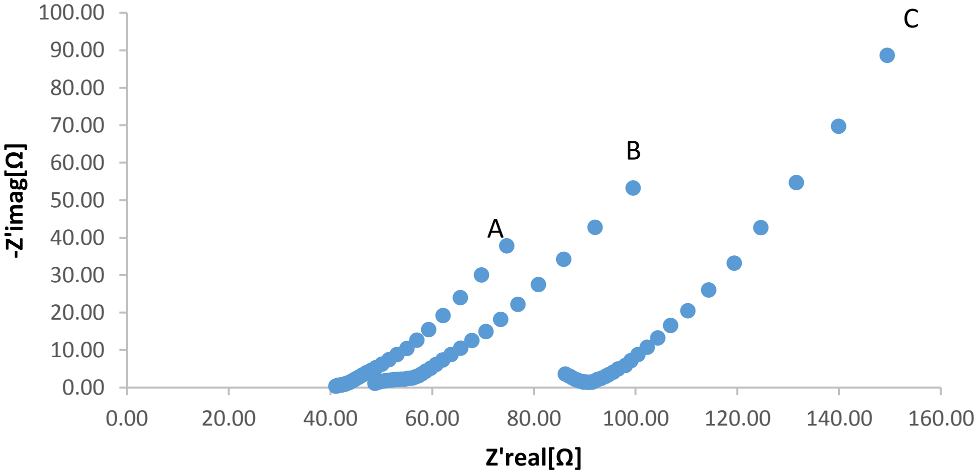

Fig.3. The internal resistance of MDCs**.** Where A is the initial internal resistance of the three-chamber MDC, B is the final internal resistance of the three-chamber MDC and as well, the initial internal resistance of the newly developed MDC, and C is the final internal resistance of the newly developed MDC

2.2.2 Peak Power and Current Densities, and Energy Productions

The maximum current and power densities produced by the newly developed MDC where 1.75 ± 0.11 A/m^3 and 0.622 ± 0.13 W/m^3 per anode volume respectively (Fig. 4) while those of the three-chamber MDC where 1.24 ± 0.30 A/m^3 and 0.35 ± 0.70 W/m^3 respectively (Fig. 5). The higher maximum current and power densities of the newly developed MDC were attributed to its higher peak voltage production as indicated earlier (Fig 1). The current densities produced by both MDCs investigated in this study were however lower than the 2.75 A/m^3 reported by Kokabien and Gude [8]. Also, the power densities produced were lower than the 8.0 W/m^3 reported by Luo et al [2]. The comparatively lower current and power densities recorded in this study could be due to voltage losses as illustrated in the polarization curves in figures 4 and 5. For maximum power to be obtained from a bioelectrochemical system, voltage losses must be kept to the minimum as current production is increased [14]. This requires that MDCs are optimized in designs and operational conditions. Also, a comparison of energy productions between MDCs investigated in this study showed that the newly developed MDC could produce more energy. The maximum energy produced by it was 21.82 J while that of the three-chamber MDC was 13.89 J. The higher energy production potential of the newly developed MDC was attributed to its higher voltage and power density productions (Fig. 1 and 4 respectively).

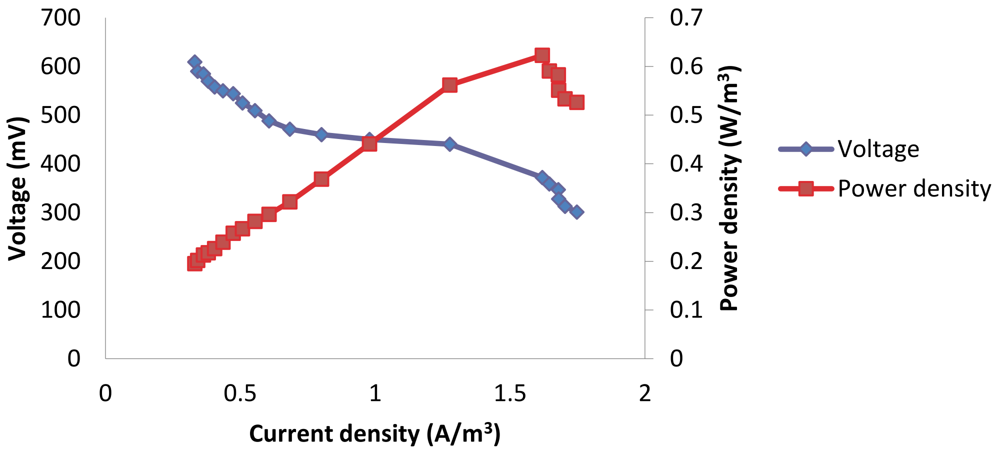

Fig.4. Polarization and power density curves of the newly developed MDC

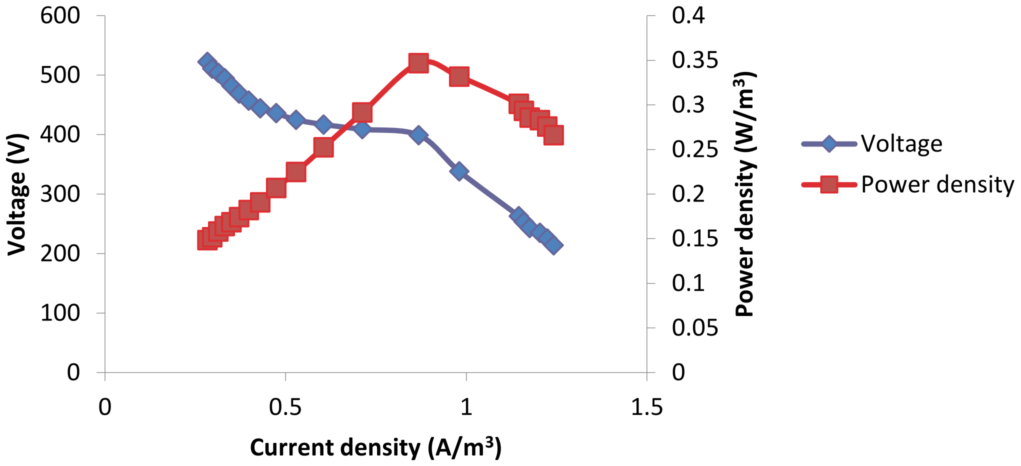

Fig.5. Polarization and power density curves of the three-chamber MDC

2.3 Desalination Efficiency of the MDCs

The total percentage desalination after three (3) batches of anolyte and catholyte replacement cycles was 50.01% for the newly developed MDC and 46.66% for the three-chamber MDC. Desalination was largely attributed to electricity production by exoelectrogens. The production of electricity in MDCs leads to the separation and movement of Na^+ and Cl^- ions out of the desalination chamber into adjacent chambers thereby causing desalination [3]. Aside from desalination due to electricity production, it was also found that water flux contributed to the desalination efficiency of the newly developed MDC. That is, the movement of water from the neutralization chambers into anolytes and catholytes increased the concentration gradient between the electrode chambers and the desalination chamber thereby causing water osmosis from the electrolytes into the desalination chamber. The dilution effect on desalination in the newly developed MDC was confirmed by the increase in the volume of water in the desalination chamber from an initial of 75 cm^3 to ~77 cm^3 at the end of the experiment. In an earlier study, Ping and He [11] also found dilution due to osmosis as a contributing factor to desalination and attributed it to the concentration difference between the anolyte and salt solution in the desalination chamber.

2.4 COD Reduction Efficiencies

The newly developed MDC provided a better wastewater treatment efficiency than the three-chamber MDC. It produced a 63.42% COD reduction efficiency from an initial COD concentration of 645 ± 2.3 mg/l whiles the three-chamber MDC produced a COD reduction efficiency of 42.81%. Reductions in COD were associated with anaerobic microbial utilization of substrate (acetate) for growth. The better COD reduction efficiency of the newly developed MDC was possibly due to the contribution of facultative anaerobes to the degradation of substrates in the anode chamber. The water fluxed from the neutralization chamber into the anode chamber possibly contained molecular oxygen thus creating anoxic conditions for the thriving of facultative anaerobes. In the presence of molecular oxygen, the facultative anaerobes would degrade substrates using the available oxygen molecules. Earlier studies have also reported that the presence of oxygen in the anode chamber contributes to the oxidation of substrates [5, 15].

3. EXPERIMENTAL

3.1 Construction of MDCs

MDCs used in this study were carved from polyoxymethylene cylinders and held together with cylindrical gaskets (Fig 6 and 7). Their individual units were clamped together with stainless steel bolts and nuts. The internal anode and cathode volumes of the MDCs were 230 cm^3 each while the volume of the desalination chambers was 77 cm^3 each. Their anode chambers were separated from desalination chambers by Anion Exchange Membranes (AEM) and the cathode chamber, Cation Exchange Membranes (CEM). Electrode materials used for both anodes and cathodes were carbon fiber-fill material (0.984” brush part, 400,000 tips per square inch, Mill-Rose, USA). The fundamental difference between the MDCs used in this study was that one used water (dilution from neutralization chambers) for pH control and the other used potassium phosphate buffer. The MDC (newly developed) relying on dilution for pH control had additional two chambers labeled the neutralization chambers. One adjacent to the anode chamber and the other, the cathode chamber. The neutralization chambers both had internal volumes 150 cm^3 each. The neutralization chamber to the end of the anode was separated from it by a CEM while that to the end of the cathode, AEM. The purpose of the neutralization chambers was to hold water for the dilution of H^+ and OH^- concentrations in anolytes and catholytes respectively. The dilution effect was based on the principle of water osmosis resulting from the concentration difference between anolytes and catholytes, and the distilled water in the neutralization chambers.

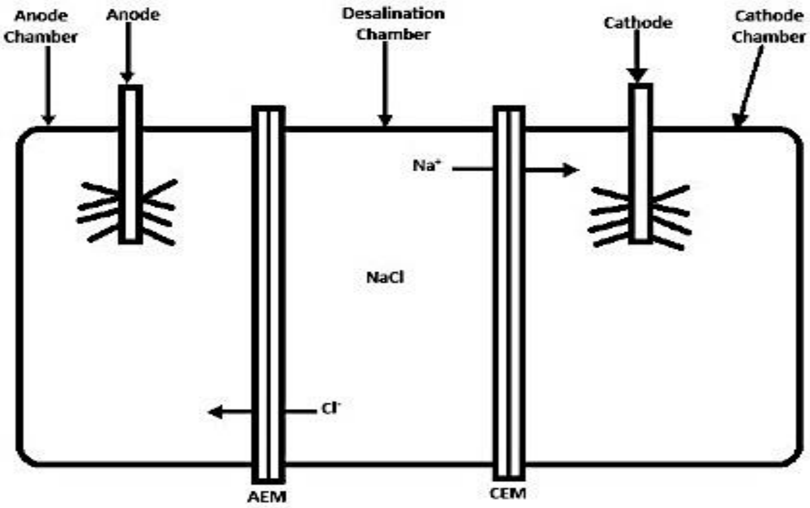

Fig.6. The three-chamber MDC with potassium phosphate buffer for pH control

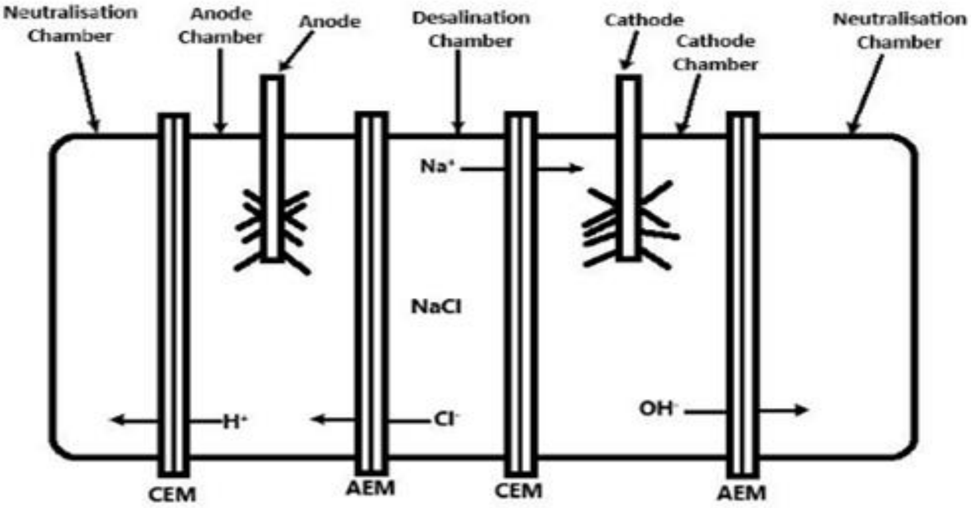

Fig.7. The newly developed MDC with neutralization chambers for pH control

3.2 Experimentation, Analysis, and Calculations

The anolyte of the three-chamber MDC comprised of 3 g/l sodium acetate in 150 ml simulated wastewater produced from a mixture of cow dung and rumen contents. This was amended with a 20 ml mineral solution (5 g/l NH_4Cl and 2.5/l NaCl) and a 50 ml potassium phosphate buffer solution (1.07 g of K_2HPO_4 and 0.53 g of KH_2PO_4 per liter distilled water [16], pH - 7.12). This resulted in a total anolyte volume of 220 ml. This MDC's total catholyte volume was also 220 ml comprising of 170 ml of 16.5 g/L potassium ferricyanide ($K_3[Fe(CN)_6)$) solution buffered with 50 ml potassium phosphate buffer solution [16]. The anolyte and catholyte of the newly developed MDC had a similar composition as those of the three-chamber MDC except that, the anolyte and catholyte of this MDC were not buffered with potassium phosphate buffer because it relied on dilution for pH control. Thus, the newly developed MDC worked on anolytes comprising of 20 ml mineral solution in 200 ml of wastewater and catholyte, 220 ml of potassium ferricyanide solution. Its' neutralization chambers contained 100 ml each of distilled water. The desalination chamber of both MDCs was supplied with 75 ml of 35 g/l NaCl solution. Both MDCs anolytes were inoculated with pre-acclimated bacteria as described by Cao et al [3]. Voltages, electrical conductivity, pH, DO, COD, current, power, desalination efficiency, volumetric current and power densities, and internal resistance were estimated as previously described [17]. Energy production was computed as; Energy (W) = Power (W/m^3) x Volume (m^3) x time (h) x 3600 s h^{-1}. On average, experiments lasted 40 hours.

4. CONCLUSION

It was established that potassium phosphate buffer stabilized pH better than dilution. However, the newly developed MDC produced higher voltages, current and power densities, desalination, and COD reduction efficiencies than the three-chamber MDC. Therefore, though dilution might not have offered the best pH stabilization effect, it however did have a positive effect on the electricity generation, desalination, and wastewater treatment efficiencies of the newly developed MDC. This notwithstanding, future research studies on dilution for pH control will have to consider improving the dilution effect considering strategies including the increase in concentration gradient between the neutralization chambers and the electrode chambers.

5. ACKNOWLEDGEMENT

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